DISSIPATION OF CAPTAN RESIDUES ON GRAPE FOLIAGE IN CALIFORNIA

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SUMMARY

The Worker Health and Safety Branch (WH&S) collected foliage samples from three grape vineyards in Kern County after applications of Captan/Sulfur 15/40 dust from July through October 1988 with an initial sampling date of July 14. This study was conducted in order to characterize the foliar deposition and dissipation rate of captan (cis-N-((trichloromethyl)thio)-4-cyclohexene-1,2-dicarboximide) following application of a dust formulation for field worker exposure estimates. Residue data from site 1 indicates captan was not applied and therefore data was not analyzed. Treatment rates per acre for the remaining two fields, designated site 2 and site 3, were 4.50 Lbs. and 3.75 Lbs. active ingredient of captan respectively. These fields were sampled weekly until harvest. Mean foliar residues for the two sites found at the beginning of the sampling were 1.28, and 1.60 micrograms per square centimeter (ug/cm^2). These two sites showed a significant correlation ($p<0.05$) to residues over time. The half-life calculated for these two sites was found to be 12 and 13 days.

INTRODUCTION

This study was conducted in order to characterize initial deposition and/or foliar residues of a dust formulation of captan on grape foliage. Captan (cis-N-((trichloromethyl)thio)-4-cyclohexene-1,2-dicarboximide) is stable in dry conditions but degrades rapidly in soil (Giles and Gilett, 1979) and is rapidly hydrolyzed in water (Mabey and Mill, 1978). Captan has a half-life of 2.5 hours in water (pH 7). Captan has a very low acute toxicity with an oral LD_{50} in the rat of >15g/kg, (Merck 1976). It is also a moderate eye irritant. Captan is a broad spectrum protectant-eradicant fungicide used on a number of fruit and vegetable crops, plant seeds, and non-food products. It is used on grapes to control dead arm, downy mildew and black rot and is applied one to three times per season.

Captan has been under review by both the federal Environmental Protection Agency under its special review process and the California Department of Pesticide Regulation under The Birth Defects Prevention Act of 1984 (Fong and Krieger, 1990). In 1987 this branch conducted degradation studies of captan residues on strawberry and grape foliage (Spencer et al., 1988). The present study was undertaken to obtain additional information about foliar residues on grapes.

MATERIALS AND METHODS

With the assistance of the Kern County Agricultural Commissioner's staff, cooperation was obtained from growers and pest control operators who would be using captan during the 1988 grape growing season. All applications were delivered by ground dusting rigs using Captan/Sulfur 15-40 Dust, (EPA# 239-167-8279 AA). The application rates for the two data sets were 30 lbs. of product corresponding to 4.5 Lbs. active ingredient (a.i.); and 25 Lbs. of product with 3.75 Lbs. a.i.. These rigs are designed with a hopper into which the dust formulation is added. The dust is blown upward through two vents which open approximately seven feet above the ground.

Sites were sampled at approximately weekly intervals beginning 1 or 3 days post-application until the day of harvest. The sampling strategy was a variation of the method described by Iwata et al. (1977). Circular leaf discs were cut using a 2.54-cm leaf punch fitted with a four-ounce glass jar.

The area to be sampled was divided into sections. Three to six rows (depending on the field size) were randomly selected prior to the initiation of sampling and marked with flagging tape for sampling. Approximately 20 vines, with the rows running west to east, were sampled from each section. Two leaf discs were taken one from each side of the vine, for a total of 40 discs per sample per row. All samples were collected in a four-ounce glass jar. Once collected, each sample jar was sealed with aluminum foil, capped and stored on ice. Samples were then shipped to California Department of Food and Agriculture Chemistry Laboratory Services in Sacramento for analysis.

SAMPLE ANALYSIS

Leaf samples were extracted according to Gunther et al. (1973). Dislodgeable residues were removed by rinsing the leaf surfaces three times using a water-surfactant solution (80 mg/L dioctyl sodium sulfosuccinate), then extracted from the aqueous solution with ethyl acetate. Samples were analyzed using an HP 5880A gas chromatograph equipped with an electron capture detector. The sample was analyzed under isothermal conditions with a column temperature of 195°C with injector at 225°C and detector at 350°C. The resulting retention

time was 5.63 minutes. The limit of detection was 0.0005 micrograms per square centimeter of leaf surface, with a 98 percent recovery.

DATA ANALYSIS

Data were analyzed using linear least squares regression of the log to the base 10 of the foliar dislodgeable residues versus time post-application. Quattro® Pro for Windows, version 5.0 was used for data analysis. A 0.05 level of statistical significance was selected. Half-life data was rounded to the nearest day. Two outliers, defined as two standard deviations from the mean, were excluded from the regression analysis for site 3. In addition, in order to be more consistent with the data collected from site 2 data from site 3, pertaining to collection dates beyond 31 days were excluded from analysis.

RESULTS

Pre-application samples showed no detectable captan residues. Table I displays the results of the sampling for the three sites after application. Table II displays the data used for calculating the half-lives for site 2 and site 3. Actualy sample results indicate initial dislodgeable captan residues ranged from 2.14 ug/cm ^{2} to 0.69 ug/cm ^{2} on the initial sampling date.

Results of data analysis showed a regression correlation coefficient for sites 2 and 3 (r^2 = 0.76, 0.53 for sites 2 and 3, respectively). Half-lives of 12 days for site 2 and 13 days for site 3 were calculated.

DISCUSSION

In the study conducted by Spencer et al., 1988, the estimated half-life for captan WP on strawberry foliage was 7.5 $\pm$ 3 days (n=6) at a rate of 4 lbs. ai/acre. Spencer et al., 1988, also conducted sampling on grape foliage but only two fields were sampled within one week of the application. Therefore no direct comparison can be made. Other studies have shown (Fong and Krieger, 1990) that in wet conditions the half-life of captan on apple leaves is approximately 4 to 7 days and may increase to 20 days in dry conditions. On strawberry foliage the captan half-life ranged from 2 to 20 days and for peaches, grapes and tomatoes, the half-life was 43, 43, and 32 days, respectively.

In the present study, the half-life of captan on grapes was calculated to be 12 and 13 days at 4.5 Lbs. and 3.75 Lbs. a.i./acre, respectively.

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TABLE 1

Captan Dislodgeable Residue - Grapes (ug/cm2)

*Site 1

INTERVAL	A	B	C	MEAN	SD
24 Hours	0.15	0.05	0.05	0.08	0.05
7 Days	0.11	0.09	0.09	0.09	0.01
14 Days	0.05	0.03	0.02	0.03	0.01
22 Days	0.27	0.15	0.04	0.06	0.09
28 Days	0.33	0.22	0.07	0.20	0.11
35 Days	0.16	0.05	0.03	0.08	0.06
42 Days	0.11	0.12	0.03	0.09	0.04
46 Days	0.13	0.11	0.03	0.09	0.04

*Data not included in report results as it appears that no application took place

Site 2 Dusted on 08/02/88

INTERVAL	A	B	C	D	MEAN	SD
Immediate Post	0.38	1.71	2.14	0.90	1.28	0.79
7 Days	2.36	1.62	0.85	0.27	1.28	0.91
14 Days	2.76	1.64	0.36	0.36	1.44	1.02
22 Days	1.70	0.83	1.02	0.19	0.94	0.62
28 Days	1.26	0.80	0.73	0.18	0.74	0.44
35 Days	0.22	0.19	0.27	0.08	0.19	0.08

Site 3 Dusted on 07/14/88

INTERVAL	A	B	C	D	E	F	MEAN	SD
Pre-Application	N.D.	N.D.	N.D	N.D.	N.D	N.D.		
12 Hours	N.T.	1.43	N.T.	N.T.	N.T.	N.T.		
3 Days	0.73	1.59	1.94	1.86	2.78	0.69	1.60	0.74
13 Days	0.54	0.43	0.22	0.26	0.57	0.62	0.44	0.16
14 Days	0.40	0.47	0.26	0.30	0.67	0.48	0.43	0.16
18 Days	0.10	0.73	0.12	0.68	0.94	0.32	0.48	0.38
24 Days	0.14	0.41	0.13	0.42	0.63	0.23	0.33	0.21
31 Days	0.17	0.41	0.34	0.40	1.04	0.34	0.45	0.33
41 Days	0.14	0.43	0.28	0.32	N.T.	N.T.	0.29	0.17
48 Days	0.11	0.25	0.23	0.19	1.04	0.23	0.34	0.38
55 Days	0.06	0.20	0.07	0.28	0.24	0.26	0.18	0.10
62 Days	0.09	0.17	0.11	0.28	0.50	0.19	0.22	0.17
64 Days	0.01	0.21	0.35	0.12	0.53	0.09	0.23	0.18
80 Days	0.03	0.16	0.20	0.10	0.26	0.03	0.13	0.09
86 Days	0.03	0.22	0.22	0.13	0.20	0.03	0.15	0.08

N.D. - Not Detected
N.T. - Not Taken
MDL - Minimum Detectable Level 0.0005 ug/cm ^{2}

Table II

Captan Dislodgeable Residue - Grapes (ug/cm2)
Calculated Half-live for Site 2 and Site 3

Site 2 Dusted on 08/02/88

	A	B	C	D
0 Days	(0.38)	1.71	2.14	0.90
7 Days	2.36	1.62	0.85	0.27
14 Days	2.76	1.64	1.00	0.36
22 Days	1.70	0.83	1.02	0.19
28 Days	1.26	0.80	0.73	0.18
35 Days	0.22	0.19	0.27	0.08
Half-Life	8.8	12.4	15.7	12.2

Mean Half-Life = 12.3 (Days)
() Parenthesis indicates result fell outside 2 standard deviations from the mean and was not used.

Site 3

	A	B	C	D	E	F
3 Days	0.73	1.59	1.94	1.86	2.78	0.69
13 Days	0.54	0.43	0.22	0.26	0.57	0.62
14 Days	0.40	0.47	0.26	0.30	0.67	0.48
18 Days	0.10	0.73	0.12	0.68	0.94	0.32
24 Days	0.14	0.41	0.13	0.42	0.63	0.23
31 Days	0.17	0.41	0.34	0.40	(1.04)	0.34
Half-Life	10.8	16.7	10.9	17.7	10.7	12.6

Mean Half-Life = 13.2 (Days)
() Parenthesis indicates result fell outside 2 standard deviations from the mean and was not used.

APPENDIX I

CAPTAN

This method is for the determination of dislodgeable captan residues from leaf surfaces.

ANALYSIS:

1. Add 50 mls of distilled water and 0.2 ml Sur-ten(80 mg/L sodium dioctyl sulfosuccinate) solution to the jar containing the leaf punches.
2. Rotate the jar for 20 minutes.
3. Decant the aqueous solution into a separatory funn el.
4. Repeat steps 1-3 twice more.
5. Add grams of NaC1 to the sep. funnel and shake to dissolve.
6. Extract the aqueous solution with 50 mls of Ethyl Acetate, draining the solvent through glass wool and Na_2SO_4 into a graduated cylinder.
7. Extract the aqueous solution twice more with 25 mls of Ethyl acetate, combining all extracts in the same cylinder.
8. Bring the final volume in the cylinder up to 10 mls.

Gas chromatograph - HP 5880A.
Oven temperature - 195 C.
Injector temperature - 225 C.
Detector temperature - 350 C.
For capillary configuration:
Column pressure - 15 PSI.
Split vent - 50 mls/min.
Septum purge - 2 mls/min.
ECD make-up gas flow - 30 mls/min.

Using these conditions, Captan has a retention time of 5.63 minutes.

Results are reported as micrograms of captan per square centimeter per sample.

Recovery: 10 ugs Captan - 98%